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(54) Title: <b>AQUEOUS TWO-STAGE EMULSION POLYMERS, BLENDS AND COATINGS THEREOF AND METHOD OF MAKING THE SAME</b>			
(57) Abstract			
<p>An aqueous two-stage emulsion polymer is disclosed having a first stage polymer with a calculated glass transition temperature of at least 70 °C, a second stage polymer having a calculated glass transition temperature between about 5° to 50 °C and a wet adhesion promoting monomer in the second stage monomer. Also disclosed are polymer blends of the two-stage emulsion polymer, coating compositions containing the two-stage polymer emulsion or polymer blend and a method for preparing the two-stage emulsion polymer.</p>			

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TITLE

10                   AQUEOUS TWO-STAGE EMULSION POLYMERS,  
                  BLENDS AND COATINGS THEREOF  
                  AND METHOD OF MAKING THE SAME

BACKGROUND OF THE INVENTION

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Field of the Invention

This invention relates to an aqueous two-stage emulsion polymer composition, polymer blends of the two-stage 20 emulsion polymer and a coating composition containing the two-stage emulsion polymer or polymer blends thereof. The invention also relates to a method for preparing the two-stage emulsion polymer compositions.

The coating compositions of this invention provide a 25 high gloss coating or film having excellent performance properties, e.g., such as hardness, wet adhesion and block resistance.

Related Background Art

30

Multi-staged or core/shell emulsion polymer compositions are well known. These staged polymer compositions are manipulated by varying the monomer composition of each stage during the emulsion 35 polymerization process in an attempt to obtain certain desirable attributes. For example, U.S. Patent No.

4,455,402 describes a two-stage polymer prepared by emulsion polymerizing a soft first stage, i.e., a polymer having a glass transition temperature, ( $T_g$ ), below 15° C, and then a hard second stage, i.e., a 5 polymer having a glass transition temperature having a  $T_g$  of at least about 60° C, in the presence of a coalescent solvent. This emulsion is said to have a low minimum filming temperature while forming films having superior early block resistance and high 10 temperature hardness.

Similar properties are said to be achieved by a process for preparing an aqueous polymer dispersion containing a two-stage emulsion polymer having a soft core and a 15 hard shell described in U.S. Patent No. 4,654,397. About 0.5 to 10 parts by weight of a monoolefinically unsaturated monomer having carboxyl and/or carboxamide functionality is included in the core, while monoolefinically unsaturated ureido compounds are 20 suggested for inclusion in the shell polymer.

U.S. Patent No. 4,683,269 describes a polymeric binder which is a mixture of homogeneous film-forming polymeric particles and heterogeneous core-shell 25 polymers for use in a coating composition that form opaque films. The core-shell polymer, which is prepared in-situ with the film-forming polymeric particles, is comprised of a core containing polymer which has a  $T_g$  that is greater than 80°C and a shell 30 polymer with a  $T_g$  that is typically less than 45°C. The opaque films are said to have improved contrast ratio and scrub properties compared to similar polymeric binders that are not formed in-situ.

35 Staged emulsion polymerization has also been employed to provide structure reinforced latex particles for use in pressure adhesive formulations such as disclosed in

U.S. Patent No. 4,717,750. A three-stage monomer feed addition is described where the second stage polymer would have a  $T_g$  greater than the first and third stage polymers. It is asserted that the latex particles

5 provide the adhesive formulations good tensile properties without a corresponding reduction in elongation properties.

U.S. Patent No. 5,021,469 describes a binder for use in

10 water based gloss paints which are said to have a low minimum film-forming temperature, a high blocking point, high gloss and good adhesion properties. The essential constituent of the binder is a multiphase emulsion polymer having a hard core with a  $T_g$  over 40°C,

15 preferably 90° to 150°C, and a soft shell with a  $T_g$  below 70°C, preferably 0° to 50°C. The soft shell requires monomers having carboxyl groups in an amount of at least 4% by weight of the polymer shell and preferably a nitrogen-containing adhesive monomer.

20

U.S. Patent No. 5,344,675 describes a blend of at least two emulsion polymers one of which is a multistage polymer having a soft stage polymer and a hard stage polymer. To reduce the need for coalescent solvent in

25 the coating formulation, the multistage polymer comprises from about 95 to 55 percent by weight of a soft stage polymer having a  $T_g$  less than about 20°C and from about 5 to 45 percent by weight of a hard stage polymer having a  $T_g$  greater than about 20°C. The

30 addition of the second emulsion polymer to the multistage polymer is said to increase hardness, block resistance and print resistance of the resulting coating.

35 While many multi-stage emulsion polymers have been described in the prior art, there is a continuing need for emulsion polymers which can provide a relatively

high gloss coating or film having excellent performance properties such as wet adhesion and block resistance.

SUMMARY OF THE INVENTION

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This invention relates to an aqueous two-stage emulsion polymer comprising:

(a) a first stage polymer having a calculated glass transition temperature of at least 70°C which is 10 an addition polymer of at least one ethylenically unsaturated monomer; and

(b) a second stage polymer having a calculated glass transition temperature of from about 5 to about 50°C which is an addition polymer of at least one 15 ethylenically unsaturated monomer polymerized in the presence of the first stage polymer, said second stage polymer further including at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate when the emulsion 20 polymer is used in a paint composition and provided that said second stage polymer contains less than 4% by weight of ethylenically unsaturated monomer having carboxylic acid functionality; in

(c) an aqueous medium;

25 wherein the weight ratio of the first stage polymer to the second stage polymer is in the range of from about 10:90 to 50:50 and the emulsion polymer has an average number particle size in the range of from about 60 to 250 nanometers. The aqueous two-stage emulsion polymer 30 may be employed in coating compositions, such as paint compositions, to provide relatively high gloss coatings having good block resistance and excellent wet adhesion characteristics.

35 The invention also relates to emulsion polymer blends comprising the above-described two-stage polymer and a resin-fortified emulsion polymer prepared with a low

molecular weight acid functional support resin.

Surprisingly, it has been discovered that such emulsion polymer blends, when employed in coating compositions provide a relatively high gloss film having good wet

5 adhesion and excellent early block resistance compared to films derived from coating compositions containing the two-stage polymer alone.

Another aspect of the invention is directed to a method

10 for preparing a two-stage emulsion polymer. The invention further relates to coating compositions containing the two-stage polymer or polymer blends of this invention. Such coating compositions include paints, varnishes and the like.

15

#### DETAILED DESCRIPTION OF THE INVENTION

The two-stage emulsion polymer of this invention may be advantageously employed in a coating composition to

20 provide a relatively high gloss coating having good blocking resistance and wet adhesion properties. A preferred aqueous two-stage emulsion polymer of this invention comprises (a) a first stage polymer having a calculated glass transition temperature of at least

25 70°C which is an emulsion polymerized addition polymer of at least one ethylenically unsaturated monomer having an average particle size in the range of from about 40 to 100 nanometers; and (b) a second stage polymer having a calculated glass transition

30 temperature of from about 5 to about 50°C which is an addition polymer of at least one ethylenically unsaturated monomer polymerized in the presence of the first stage polymer, said second stage polymer further including at least one ethylenically unsaturated

35 monomer having a functional group that promotes adhesion to a substrate when the emulsion polymer is used in a paint composition and provided that said

second stage polymer contains less than 4% by weight of ethylenically unsaturated monomer having carboxylic acid functionality; in (c) an aqueous medium; wherein the weight ratio of the first stage polymer to the

5 second stage polymer is in the range of from about 10:90 to 50:50 and the emulsion polymer has an average number particle size in the range of from about 60 to 250 nanometers.

10 The ethylenically unsaturated monomers employed in the present invention have at least one polymerizable carbon-to-carbon unsaturated bond. These compounds are well known and include, for example, C<sub>2</sub> to C<sub>20</sub> alkenes, C<sub>3</sub> to C<sub>20</sub> alkadienes, C<sub>5</sub> to C<sub>20</sub> alkatrienes, C<sub>5</sub> to C<sub>20</sub>

15 cycloolefins, vinyl substituted aromatics, acrylic or methacrylic acid, C<sub>1</sub> to C<sub>20</sub> alkyl esters of acrylic acid or methacrylic acid, C<sub>6</sub> to C<sub>20</sub> aryl esters of acrylic or methacrylic acid, C<sub>7</sub> to C<sub>20</sub> aralkyl esters of acrylic or methacrylic acid and the like. Styrene, C<sub>3</sub>-C<sub>20</sub> acrylates

20 and C<sub>3</sub>-C<sub>20</sub> methacrylates are preferred examples of ethylenically unsaturated monomers used in this invention. Other useful monomers will be readily apparent to those skilled in the art.

25 Exemplary ethylenically unsaturated monomers which are suitable crosslinking agents for use in this invention include, without limitation, divinyl benzene, hexanediol diacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylol propane

30 triacrylate, trimethylol propane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, polyethylene glycol diacrylate and polyethylene glycol dimethacrylate and the like.

35 The calculated glass transition temperature of each polymer stage is determined using the Fox equation , see e.g., "Introduction to Physical Polymer Science,"

L.H. Sperling, John Wiley and Sons, 1986. The calculation is made on the ethylenically unsaturated monomers comprising a particular stage of the two-stage emulsion polymer exclusive of any cross linking agents, 5 adhesion promoters or any other additives. Calculation of the glass transition temperature using the Fox equation is well known to those skilled in the art.

The first stage polymer of this invention has a 10 calculated glass transition temperature of at least 70°C, i.e., it is a hard polymer stage. Particularly preferred ethylenically unsaturated monomers useful in the first stage include methyl methacrylate, styrene and alpha-methyl styrene. Other ethylenically 15 unsaturated monomers that may be employed will be readily apparent to those skilled in the art. Most preferably, the first stage polymer has a calculated glass transition temperature of at least 80°C.

20 The second stage polymer of this invention has a calculated glass transition temperature between about 5° to about 50°C, i.e., it is a soft polymer stage. Particularly preferred ethylenically unsaturated monomers useful in the second stage include alkyl 25 acrylates and methacrylates such as methyl methacrylate, n-butyl acrylate, 2-ethylhexylacrylate and n-butylmethacrylate. The second stage polymer may contain ethylenically unsaturated monomer having carboxylic acid functionality, such as acrylic acid or 30 methacrylic acid and the like, in an amount less than 4% by weight of the second stage polymer. Preferably, the second stage polymer contains one or more ethylenically unsaturated monomers having carboxylic acid functionality, the total amount of which is 35 between about 0.05% to about 3.9% by weight of the second stage polymer.

The second stage monomer also contains at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate when the emulsion polymer is used in a paint composition i.e., a 5 wet adhesion promoting monomer. The wet adhesion promoting monomer is present in the second stage polymer generally in an amount of from about 0.5 to about 1.5 percent by active weight, based on the total active weights of the first stage and second stage 10 monomers.

The wet adhesion promoting monomers are ethylenically unsaturated, free-radically polymerizable monomers typically having an amino, ureido, or N-heterocyclic 15 group, such as dialkylaminoalkyl esters and dialkylaminoalkyl amides of acrylic acid and/or methacrylic acid, and particularly those having from 1 to 5 carbon atoms in the alkyl groups, and free radically polymerizable compounds of urea, ethylene 20 urea, or propylene urea such as described in U.S. Patent No. 5,021,469, the disclosure of which is incorporated by reference herein.

Wet adhesion promoting monomers that may be employed in 25 this invention include, for example, dimethylaminoethyl acrylate and methacrylate, diethylaminoethyl acrylate and methacrylate, dimethylaminopropyl acrylate and methacrylate, 3-dimethylamino-2,2-dimethylpropyl-1- acrylate and methacrylate, 2-N-morpholinoethyl acrylate 30 and methacrylate, 2-N-piperidinoethyl acrylate and methacrylate, N-(3-dimethylaminopropyl)acrylamide and methacrylamide, N-(3-dimethylamino-2,2- dimethylpropyl)acrylamide and methacrylamide, N- 35 dimethylaminomethyl acrylamide and methacrylamide, N-(4-morpholino-methyl) acrylamide and methacrylamide, vinylimidazole, vinylpyrrolidone, N-(2-

methacryloyloxyethyl)ethylene urea, N-(2-methacryloxyacetamidoethyl)-N', N'-ethylene urea, allylalkyl ethylene urea, N-methacrylamidomethyl urea, N-methacryoyl urea, N-[3-(1,3-diazacyclohexan-2-on-5-propyl) methacrylamide, 2-(1-imidazolyl)ethyl methacrylate, and 2-(1-imidazolidin-2-on)ethyl methacrylate.

Particularly preferred wet adhesion monomers include  
10 those having a ureido group, such as methacrylamidoethylethylene urea, available as Sipomer Wam® II from Rhône-Poulenc, Princeton, New Jersey.

Generally the weight ratio of the first stage polymer  
15 to the second stage polymer is in the range of from about 10:90 to 50:50, preferably about 15:85 to 40:60. The emulsion polymer typically has an average number particle size in the range from about 60 to 250 nanometers, preferably about 70 to about 150  
20 nanometers.

The particle size of the emulsion polymers of this invention are typically measured by laser scattering, using a Brookhaven Instrument Corp. BI90 instrument  
25 technique. Other known particle size measurement techniques which may be employed, if desired, include capillary hydrodynamic fractionation or size exclusion chromatography.

30 Another aspect of this invention relates to a method for making the above-described aqueous two-stage emulsion polymers. This method comprises emulsion polymerizing at least one ethylenically unsaturated monomer to form a first stage polymer wherein the first  
35 stage polymer has a calculated glass transition temperature of at least 70°C and an average number particle size of from about 40 to 100 nanometers.

It is preferable to practice the method by introducing a precharge of the first stage pre-emulsion composition into a reaction vessel in which the emulsion polymerization is to be conducted in order to generate

5 a seed particle prior to adding the remainder of the first stage monomer composition charge. Generally, the precharge is about 5 to about 15 percent by weight of the total weight of the first and second stage monomers. Generation of a seed particle provides a

10 means to control the particle size of the emulsion polymer. The seed particles can be added directly to the reactor, i.e., prepared in a separate reaction, or generated in-situ as described above. The reactor precharge may be followed or preceded by an initiator

15 charge and then a hold period. After the seed particles have been generated, then the first stage pre-emulsion composition is fed to the reactor along with an (optionally) initiator co-feed. After completion of the first stage pre-emulsion feed, the

20 second stage monomer is fed to the reactor along with an optionally and most preferably initiator co-feed to generate the two-stage emulsion polymer of this invention.

25 The second stage polymer is formed by emulsion polymerizing in the presence of the first stage polymer at least one ethylenically unsaturated monomer and at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate

30 when the emulsion polymer is used in a paint composition, wherein the calculated glass transition temperature, exclusive of the monomer that promotes adhesion, is in the range from about 5° to about 50°C. In addition, the second stage polymer preferably

35 contains an ethylenically unsaturated monomer having a carboxylic acid functionality, so long as the ethylenically unsaturated monomer having carboxylic

acid functionality is present in an amount less than 4% by weight of the second stage polymer.

The polymerizable feed compositions and the 5 polymerization reactor can contain in the usual known amounts, dispersion aids, emulsifiers, photosensitizers, colorants, initiators, catalysts, chain transfer agents and other additives conventionally used in polymerization reactions, all of 10 which are known, as are their uses.

Any of the known dispersion agents can be used at the conventional concentrations, including, for example, hydroxyethyl cellulose, carboxymethyl cellulose, 15 poly(vinyl alcohol), methyl cellulose, sulfated cellulose, and the like.

Any of the known emulsifiers or surfactants can be used at a total concentration preferably between about 1.0 20 and about 5.0 percent by weight active material based on the total weight of polymerizable reactants charged. These include anionic, cationic, nonionic and copolymerizable surfactants, with a nonionic/anionic surfactant mixture being most preferred. Among the 25 useful emulsifying agents there are included soaps, sulfonated alkylbenzenes, alkylphenoxyethyl sulfonates, sodium lauryl sulfonate, salts of long chain amines, salts of long chain carboxylic or sulfonic acids, alkylphenol ethoxylates, linear alcohol ethoxylates, or 30 any other emulsifying agent or surfactant. Typically, a range of about 0 to about 30 percent by weight of the emulsifiers or surfactants may be charged to the reaction zone and about 70 to about 100 percent weight may be used in the polymerizable feed compositions.

35

Any of the known initiators may be used. These include without limitation, persulphate salts such as ammonium

persulphate, potassium persulphate or sodium persulphate, 2,2'-Azobisisobutyronitrile (AIBN), organic peroxides and the like. While initiators may be present in the polymerizable feed compositions, they 5 are most preferably employed in the initial charge of the polymerization reaction zone and by addition thereto by an aqueous cofeed in amounts well known to those skilled in the art.

10 Any of the known chain-transfer agents may be used including for example, butyl mercapto propionate; iso-octyl mercapto propionic acid; iso-octyl mercapto propionate ("IOMP"); bromoform; bromotrichloromethane ("BTM"); carbon tetrachloride; alkyl mercaptans such 15 as n-dodecyl mercaptan, tertiary-dodecyl mercaptan, octyl mercaptan, tetradecyl mercaptan, and hexadecyl mercaptan; alkyl thioglycolates such as butyl thioglycolate, iso-octyl thioglycolate, and dodecyl thioglycolate; thioesters; and combinations thereof.

20 The emulsion polymers of this invention may be produced by first combining preselected relative amounts of initiator, surfactant and aqueous medium in an agitated reactor of suitable size, and heating the agitated 25 reactor contents to a desired reaction temperature, typically 40° to 90°C, more preferably 70° to 90°C, over a predetermined period of time, which may typically be about 15 minutes. At least one optional chain-transfer agent may also be incorporated into the 30 agitated reactor contents at this time, if desired. Nitrogen or another suitable inert gas may be introduced into the reactor headspace during the heat-up of the water-surfactant mixture to eliminate oxygen from the reaction vessel, if desired. The pre- 35 emulsified monomer is charged to the water-surfactant mixture (already at the desired reaction temperature), held to regain the temperature and then the initiator

charge is added. The first and second stage emulsion polymers are then fed to the reactor as described above to produce the aqueous two-stage emulsion polymers of their invention.

5

In the preparation of certain preferred embodiments of the aqueous emulsion polymers of the invention, the aqueous medium will consist essentially of water only.

However, in the preparation of certain other 10 embodiments of the aqueous emulsion polymers of the invention, it will be desirable that the aqueous medium comprise water and at least one other water-miscible volatile organic liquid.

15 Examples of water-miscible volatile organic liquids that are useful in this regard include but are not limited to alcohols having 1 to 12 carbons; dialkyl ethers having 2 to 24 carbons, ethylene and propylene glycols and their monoalkyl and dialkyl ethers; 20 relatively low formula weight polyethylene oxides and their alkyl and dialkyl ethers (i.e., having a chemical-formula weight of less than about 200 grams per mole); and combinations thereof.

25 The aqueous two-stage emulsion polymers of this invention may also be produced using a power feed emulsion polymerization method. Such a method is described in copending application No. 08/539,808 filed October 5, 1995, entitled "Seed Polymerized Latex 30 Polymer Having A Gradient Polymeric Morphology and Process For Preparing The Same", the disclosure of which is incorporated by reference herein. In the power feed method a stage 1 polymer pre-emulsion composition (an aqueous emulsion of ethylenically 35 unsaturated monomers) is fed to the reactor under addition polymerizable conditions for a predetermined

amount of time to produce the stage 1 polymer. After the predetermined amount of time, the stage 2 polymer pre-emulsion composition (an aqueous emulsion of ethylenically unsaturated monomers) is then fed into

5 the tank holding the remaining stage 1 polymer pre-emulsion composition so that the feed from the tank to the reactor contains an increasingly greater concentration of stage 2 polymer pre-emulsion composition. Although the stage 2 polymer will have a

10 gradient morphology, that has a calculated Tg which decreases from the interior of the stage 2 polymer to the outer portion of the stage polymer, the overall average of the calculated Tg for the stage 2 polymer will be from about 5 to about 50°C, as described above.

15

The invention is also related to an aqueous emulsion polymer blend comprising the above-described aqueous two-stage emulsion polymer and a resin-fortified emulsion polymer prepared with a low molecular weight

20 acid functional support resin such as disclosed, for example, in U.S. Patent No. 5,284,894 and U.S. Patent No. 4,820,762, the disclosure of both of which are incorporated by reference herein. Resin-fortified emulsion polymers prepared with low molecular weight

25 acid functional support resins can advantageously employ a reduced level of surfactant, or may even be surfactant free, such as disclosed in U.S. Patent No. 4,151,143, the disclosure of which is incorporated by reference herein.

30

The low molecular weight acid functional support resin employed in the resin-fortified emulsion polymer generally has a molecular weight between about 4000 to about 25,000, and is a polymer of ethylenically

35 unsaturated monomers which include at least one acid functional ethylenically unsaturated monomer in an amount from about 10 to about 40 percent by weight of

the support resin. Particularly preferred acid functional ethylenically unsaturated monomers for use in the support resin include acrylic acid, methacrylic acid and the like. Generally, the remainder of the

5 support resin is comprised of ethylenically unsaturated monomers preferably having no acid functionality such as, for example, styrene,  $\alpha$ -methyl styrene, acrylic and methacrylic acid esters and the like.

10 The support resin may be prepared employing well known emulsion polymerization techniques to addition polymerize the ethylenically unsaturated monomers. The low molecular weight support resin having acid functionality is then neutralized with an amine, such as ammonia, to induce water solubility or dispersibility. Additional ethylenically unsaturated monomers having no acid functionality are then emulsion polymerized in the presence of the aqueous stabilized support resin to form the resin-fortified emulsion

15 polymer. The resin-fortified emulsion polymer may also include crosslinking agents and other additives typically employed in emulsion polymers. These resin fortified emulsion polymers may be prepared using emulsion-polymerization conditions readily apparent to

20 25 those skilled in the art.

Generally, the two-stage emulsion polymer is blended with the resin-fortified emulsion polymer prepared from an acid functional support resin in a ratio from about

30 35 60:40 to about 95:5. Such blended emulsion polymers have been found to provide relatively high gloss coatings having excellent block resistance compared to the two-stage emulsion polymer alone.

35 This invention is further related to coating compositions containing (i) the aqueous two-stage emulsion polymer of this invention or the above-

described blended emulsion polymers and (ii) a coalescing solvent. The coalescing solvents may include the above described water-miscible volatile organic liquids such as Texanol® (2,2,4-trimethyl-1,3-5 pentanediol monoisobutyrate available from Eastman Chemical, Kingsport, Tennessee), diethylene glycol monobutyl ether, ethylene glycol ethyl hexyl ether and Exxate® 1300 (a high boiling alkyl acetate of a primary alcohol available from Exxon Chemicals, Houston, 10 Texas). In addition, if the coating composition is a paint it will contain a pigment such as, for example, titanium dioxide.

Generally, the coating compositions contain the two-stage emulsion polymer in an amount of about 50 to 15 about 65 percent by weight of the coating composition. Coalescing solvents are generally present in an amount from about 2 to about 4 percent by weight of the composition. When a pigment is present, such as 20 titanium dioxide, then the amount is generally in the range from about 4 to about 25 percent by weight of the composition.

The coating compositions may also include surfactants, 25 dispersants, defoamers, thickeners, biocides and the like. Such adjuvants and their use in coating compositions are well known to those skilled in the art.

30

#### Industrial Applicability

The two-stage emulsion polymer and aqueous emulsion polymer blends of this invention are generally employed in coating compositions. These coating compositions 35 are typically paints, varnishes or any other coating composition that provides a protective finish or film

on a substrate to which the coating composition has been applied.

The Examples which follow are intended as an 5 illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

Example 1

10

An aqueous two-stage emulsion polymer was prepared in the following manner:

A stage 1 monomer pre-emulsion was prepared by first 15 adding to a monomer weigh tank deionized water (4.89 lb; 2.22 kg), Rhodapon® LCP (0.60 lb; 0.27 kg) (sodium lauryl sulfate available from Rhône-Poulenc, Princeton, New Jersey) and Tergitol® 15-5-5 (0.24 lb; 0.11 kg) ( $C_{11,15}H_{23-31}O(CH_2CH_2O)_xH$  where x is approximately 5.0; available 20 from Union Carbide, Danbury, Connecticut) with agitation to provide a uniform mixture. Next, hexanediol diacrylate (HDDA) (0.11 lb; 0.05 kg), methyl methacrylate (3.45 lb; 1.56 kg) and styrene (8.43 lb; 3.82 kg) were added with high speed mixing to form a 25 stable stage 1 monomer pre-emulsion. A stage 2 monomer pre-emulsion was prepared by adding deionized water (12.27 lb; 5.57 kg), Rhodapon® LCP (1.55 lb; 0.70 kg) and Tergitol® 15-5-15 (0.62 lb; 0.28 kg) to a monomer weigh tank and agitating to uniformity. Next, HDDA 30 (0.43 lb; 0.20 kg), Sipomer WAM® II (0.86 lb; 0.39 kg) and acrylic acid (0.086 lb; 0.39 kg) were added to the stage 2 monomer mixture, followed by the addition of methyl methacrylate (5.40 lb; 2.45 kg), 2 ethyl hexyl acrylate (5.40 lb; 2.45 kg) and n-butyl methacrylate 35 (19.42 lb; 8.81 kg). The components were mixed at high speed to form a stable stage 2 monomer pre-emulsion.

A catalyst solution was prepared by mixing deionized water (5.89 lb; 2.67 kg) and ammonium persulfate (0.15 lb; 0.07 kg). A precharge initiator solution was prepared containing ammonium persulfate (0.022 lb; 5 0.010 kg) in deionized water (0.086 lb; 0.039 kg). Then the reactor was charged with deionized water (23.72 lb; 10.76 kg) and Rhodapon® LCP (0.14 lb; 0.064 kg) and heated to about 80°C. A monomer precharge, i.e., 5.97 lb (2.71 kg) of the stage 1 monomer pre-10 emulsion was charged to the reactor and held until an 80°C reactor temperature was re-established. Next, the precharge initiator solution was added to the reactor. After 15 minutes, the addition of the stage 1 monomer pre-emulsion was started at a rate of 0.39 lb/min (0.18 15 kg/min) along with the simultaneous addition of the catalyst solution at a rate of 0.031 lb/min (0.014 kg. min). The stage 1 monomer pre-emulsion was added to the reactor over a period of approximately 30 minutes, while the catalyst solution was added for approximately 20 3.25 hours. After adding the stage 1 monomer pre-emulsion, the addition of the stage 2 monomer pre-emulsion to the reactor was begun at a rate of 0.31 lb/min (0.14 kg/min). The stage 2 monomer pre-emulsion was added over a period of approximately 2.5 hours. 25 The reactor contents were maintained at a temperature of about 80°C during the polymerization reaction. After additions of the second stage monomer pre-emulsion and catalyst solution were completed, the reactor contents were held at 80°C for 60 minutes. The 30 resulting two-stage emulsion polymer had 44.5 - 45% nonvolatile materials, an average particle size of 100-150 nanometers (measured by laser scattering using a Brookhaven Instrument Corp. BI90 (BCI)), a viscosity of 30-100 centipoise (0.03-0.1 pascal·seconds), a pH of 35 8.0 - 9.0 and a % grit (wet, % based on total latex) of 0.03%.

Example 2

An aqueous two-stage emulsion polymer was prepared 5 using a power feed emulsion polymerization process. A stage 1 monomer pre-emulsion, prepared in a manner similar to Example 1, contained deionized water (4.92 lb; 2.23 kg), Rhodapon® LCP (0.60 lb; 0.27 kg), Tergitol® 15-5-5 (0.24 lb; 0.11 kg), methyl 10 methacrylate (3.45 lb; 1.56 kg) and styrene (8.55 lb; 3.88 kg). A stage 2 monomer pre-emulsion was also prepared in a manner substantially similar to Example 1. A monomer precharge (5.92 lb; 2.69 kg) of the stage 1 pre-emulsion was charged to the reactor and the 15 reactor contents were brought to a temperature of 80°C.

Next, ammonium persulphate (20%) (0.43 lb; 0.20 kg) was charged to the reactor and the reactor was held for 15 minutes. The stage 1 pre-emulsion and a catalyst solution (0.086 lb (0.039 kg) ammonium persulfate in 20 3.37 lb (1.53 kg) deionized water) were simultaneously fed to the reactor at 0.39 lb/min (0.18 kg/min) and 0.023 lb/min (0.010 kg/min), respectively. After twenty minutes the stage 2 monomer pre-emulsion feed was started into the stage 1 monomer pre-emulsion tank 25 at 0.77 lb/min (0.18 kg/min). After completion of the feeds to the reactor, the reactor contents were held for 60 minutes at 80°C. A two-step emulsion polymer was obtained.

Example 3

A coating composition was prepared with the two-staged emulsion polymer composition of Example 1 by combining the following components:

	<u>Components</u>	<u>Wt. %</u>
	Propylene Glycol	1.91
	Dispersant	0.14
	Triton® CF-10 (surfactant)	0.22
5	Biocide	0.04
	Ammonia	0.06
	Defoamer	0.05
	DSX-1550 (associative thickener)	0.04
	TiO <sub>2</sub>	22.09
10	Two-stage emulsion polymer (Ex. 1)	63.70
	Acrysol® RM 1020 (associative thickener)	0.88
	Dehydran 1620 (defoamer)	0.18
	Texanol® (coalescing solvent)	3.46
	DSX-1514 (associative thickener)	0.27
15	Water	7.05

Triton® CF-10 Octylphenol oxypolyethoxyethylbenzyl ether available from Union Carbide, Danbury Connecticut.

20

DSX-1514® and DSX-1550® are synthetic polyurethane polymers available from Henkel Corp., Gulph Mills, Pennsylvania.

25

Acrysol RM-1020 is a synthetic polyurethane polymer available from Rohm and Haas, Philadelphia, Pennsylvania.

30

Dexhydran® 1620 is an alcohols and polysiloxane adduct mixture available from Henkel Corp., Gulph Mills, Pennsylvania.

35

Texanol® -2,2,4-trimethyl-1,3-pentanediol monoisobutyrate available from Eastman Chemical, Kingsport, Tennessee.

The resulting coating composition had non-volatile materials in an amount of 51.5% by weight and a pigment volume concentration of 17.0%.

5

Example 4A

An resin-fortified emulsion polymer prepared with a low molecular weight acid functional support resin had the following composition:

10

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Components	Wt. %
STY/AMS/AA copolymer	10.41
BA/STY/MMA/HDDA copolymer	39.55
Ammonia	2.48
Water	46.75
Tergitol® 15-S-12	0.79
Biocide	0.02
STY - styrene; AMS- $\alpha$ -methyl styrene; AA - acrylic acid; BA - butyl acrylate; MMA - methyl methacrylate; HDDA - hexanediol diacrylate	

A first resin was prepared by reacting styrene (31.08 parts),  $\alpha$ -methyl styrene (31.85 parts), acrylic acid (31.12 parts), in carbitol (5.72 parts) in a reactor at 25 a reaction temperature of about 443°F (228°C) by continuous solution polymerization followed by stripping to remove the carbitol. Then a second resin was prepared by charging water (63.5 parts) to a reactor and heating the water to 160-180°F (71-82°C) 30 followed by the addition of ammonia (28%) (6.5 parts) and the first resin (30.0 parts). The resin-fortified emulsion polymer was then prepared by first charging the above-prepared second resin (34.68 parts), Tergitol® 15-S-12 (0.79 parts) and deionized water 35 (18.55 parts) to a reactor followed by agitating and heating to about 176°F (80°C). Next, the reactor was charged with ammonium persulfate (0.27 parts) made up

as a 20% solution in water. Then, styrene (12.96 parts) was fed to the reactor for about 30 minutes while maintaining the reaction temperature at about 176°F (80°C). The reactor was then held from about 20 5 minutes. Next a monomer mixture of methyl methacrylate (2.63 parts), butyl acrylate (23.15 parts) and 1,6-hexanediol acrylate (0.53 parts) was fed to the reactor over about a 90 minute period while maintaining the reaction temperature. The reaction mixture was then 10 held for about 45 minutes at about 176°F (80°C) followed by cooling the mixture to about 120°F (49°C). Ammonium hydroxide (0.22 parts) and a biocide were then added to obtain the resin-fortified emulsion polymer prepared with a low molecular weight acid functional 15 support resin.

Example 4B

A coating composition was prepared using a blend of the two-staged emulsion polymer of Example 1 blended with 20 the emulsion polymer prepared in Example 4A. The coating composition contained the following components:

	<u>Components</u>	<u>Wt. %</u>
	Propylene Glycol	1.89
25	Dispersant	0.14
	Triton® CF-10 (surfactant)	0.22
	Biocide	0.04
	Ammonia	0.06
	Defoamer	0.05
30	DSX-1550 (thickener)	0.04
	TiO <sub>2</sub>	21.88
	Two-stage polymer emulsion (Ex. 1)	50.49
	Resin-fortified emulsion polymer (Ex. 4A)	11.64
	Acrysol® RM 1020 (thickener)	0.88
35	Dehydran® 1620	0.18

Texanol	3.41
D8X-1514 (thickener)	0.30
Water	8.77

5 The coating compositions of Examples 3 and 4B were tested for gloss, early block resistance (24 hr), block resistance (5 days) and wet adhesion properties.

Gloss

10 The coating compositions were drawn down on sealed Leneta charts and allowed to dry. Gloss was measured with a Byk-Gardner Micro-TRI-Glossmeter, after the film had dried for 24 hours. The meter was placed on top of 15 the film, and then activated to read values at 20° and 60°. (These degree values refer to the angle of incidence from the plane perpendicular to the surface of the paint fibers).

20 Block Resistance and Early Block Resistance

Block and early block resistance were tested using ASTM D-4946. The coating compositions were drawn down on Leneta charts sealed with a clear alkyd coating to 25 simulate the application of paint on a painted surface. After a 24 hour drying period (early block resistance) or a 5 day drying period (block resistance) at room temperature (room temperature block) or 120°F (hot block) two similar coated and treated cards were placed 30 against each other so that the coated side of each card was in contact with the other and a weight exerting 2 psi was placed on top of the cards. After 1 hour the weight was removed, the cards were peeled apart and a visual rating was assigned to the ease of separation. 35 Complete adhesion was designated 1 while coated cards that essentially fell apart were assigned a 10.

Wet Adhesion

Wet adhesion analysis was performed on the coating compositions of this invention using a 10' (minute) peel test, a 10' (minute) XH(crosshatch) test, a 24 hour water soak test and a CRGI scrub.

Plastic scrub charts were coated with high-gloss alkyd paint and allowed to age at least 6 weeks to no more than 6 months at ambient conditions. The, 0.003 inch (0.076 mm) films of the test paints were drawn down over the alkyd and allowed to dry for 7 days in a controlled environment at 70°F (21°C) and 50% relative humidity. These films were then tested for wet adhesion.

The 10' (minute) peel test was performed by soaking the film with tap water for 10 minutes by placing a drenched napkin on top of the film. After ten minutes, the film was quickly wiped dry. An "X" was cut into the film using a razor blade, then scratched using the finger nail of the tester. A subjective rating of from 1 to 10 (10 = no removal) was then given based on the force needed to remove the film.

25 The 10'XH (ten minute crosshatch) test was run as in the 10' peel test above immediately after the peel test. A crosshatch tape test, using ASTM D3359, was employed. The number of the rating, which in the ASTM D3359 ranges from 0 to 5, was then multiplied by two to standardize the ratings so that 10 was considered the best.

35 The CRGI test was run as follows: Using the prepared drawdowns over high gloss alkyd as referred to above, these films were immersed in tap water for 24 hours. Blistering was then noted according to ASTM D-714. Two

parallel lines were quickly cut with one inch separation, perpendicular to the path of the scrub to follow. The film was then immediately placed in an Abrasion Tester (Gardner Labs) and scrubbed in a 5 similar manner to ASTM D-2486, except using a 50% aqueous Comet® cleanser solution, and using no shim as in the ASTM test. The test reached the fail point when the film had been removed between the two parallel cuts. The number of scrub cycles was then noted.

10

The results of the above-described tests for the coating compositions of Examples 3 and 4B are set forth in Table 1 below.

Table 1

Coating Comp.	Gloss		Early Block (24 hr)		Block (5 day)		Wet Adhesion				
	20°	60°	RT <sup>1</sup>	Hot <sup>2</sup>	RT <sup>1</sup>	Hot <sup>2</sup>	10' Peel <sup>3</sup>	10° XH	WS	24h	CRG
Ex. 3	39	82	6	5	7	7	5	8		✓	2000+
Ex. 4	40	82	8	7.5	8	8	2	0	6D <sup>4</sup>	6D <sup>4</sup>	1030

1 RT = room temperature

2 120°F

3 Dense Blisters

4 XH = Crosshatch

5 WS = Watersoak ✓ - no blisters observed

These results indicate that the coating of Example 3 containing the two-stage emulsion polymer of this invention provides a reasonably high gloss and excellent wet adhesion performance. The coating of 5 example 4B, employing an emulsion polymer blend, exhibits a reasonably high gloss and excellent block resistance, although the wet adhesion properties are somewhat compromised.

10

Example 5

An aqueous two-stage emulsion polymer was prepared in a manner similar to Example 1, with the exception that seed formation was eliminated by omitting the monomer 15 precharge step. The resulting aqueous emulsion polymer had 45% non-volatile materials, a pH of 8.6, a viscosity of 23 cps (0.023 pascal·seconds) and a BIC average particle size of 157 nm.

20

Example 6

An aqueous two-stage emulsion polymer was prepared in a manner similar to Example 1, with the exception that the monomer precharge was 15% of the stage 1 monomer 25 pre-emulsion. The resulting aqueous emulsion polymer had 44.8% non-volatile materials, a pH of 8.2, a viscosity of 28 cps (0.028 pascal·seconds) and a BIC average particle size of 122 nm.

30

Comparative Example 1

An aqueous two-stage emulsion polymer was made in a manner similar to Example 1, with the exception that the adhesion promoter (Sipomer WAM® II) was not added 35 to the stage 2 monomer pre-emulsion. The resulting emulsion polymer had 44.7% non-volatile materials, a pH

of 9.1, a viscosity of 31 cps (0.031 pascal·seconds) and a BIC average particle size of 126 nm.

Comparative Example 2

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An aqueous two-stage emulsion polymer was made in a manner similar to Example 1, with the exception that the adhesion promoter (Sipomer WAM® II) was added to the stage 1 monomer pre-emulsion. The resulting 10 emulsion polymer had 45.1% non-volatile materials, a pH of 8.4, a viscosity of 27 cps (0.027 pascal·seconds) and a BIC average particle size of 96 nm.

Example 7

15

An aqueous two-stage emulsion polymer was made in a manner similar to Example 1, with the exception that the ratio of the stage 1 to stage 2 monomers was 15:85, while the amounts of adhesion promoter (Sipomer WAM® 20 II) and acrylic acid were held constant. The resulting emulsion polymer had 44.8% non-volatile materials, a pH of 8.7, a viscosity of 36 cps (0.036 pascal·second) and a BIC average particle size of 126.

25

Comparative Example 3

An aqueous emulsion polymer was prepared in a manner similar to Example 1 with the exception that the monomers were polymerized in a single stage 30 polymerization process. The resulting aqueous polymer had 44.9% non-volatile materials, a pH of 7.8, a viscosity of 37 cps (0.037 pascal·seconds) and a BIC average particle size of 114 nm.

Example 8

An aqueous two-stage emulsion polymer was made in a manner similar to Example 1, with the exception that 5 the ratio of the stage 1 to stage 2 monomer was 50:50, while the amounts of adhesion promoter (Sipomer WAM® II) and acrylic acid were held constant. The resulting aqueous emulsion polymer had 45% non-volatile materials, a pH of 7.5, a viscosity of 30 cps (0.030 10 pascal·seconds) and a BIC average particle size of 125 nm.

Comparative Example 4

15 An aqueous emulsion polymer was prepared in a manner similar to Example 1, with the exception that the calculated Tg of the stage 2 polymer was approximately -3°C. The resulting aqueous emulsion polymer had 44.8% non-volatile materials, a pH of 7.4, a viscosity of 33 20 cps (0.030 pascal·seconds) and a BIC average particle size of 116 nm.

Coating compositions were prepared using the aqueous emulsion polymers of Examples 5-8 and Comparative 25 Examples 1-4 in a manner similar to that described in Example 3. The coating compositions contained 8% Texanol coalescent solvent, 10% thickener (except Example 5 that had 15% thickener) and 17% pigment volume concentration. The gloss, block resistance and 30 wet adhesion properties of these coating compositions were determined in the manner described above. The results are set forth in Table 2.

Comparative Example 5

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An aqueous emulsion polymer was prepared in a manner similar to Example 1, with the exception that acrylic

- 30 -

acid was included in the stage 2 polymer in an amount of 4% by weight of the total monomer of the stage 2 polymer. The resulting aqueous emulsion polymer had 45.2% non-volatile materials, a pH of 5.1, a viscosity of 74 cps (0.074 pascal·seconds) and a BIC average particle size of 132 nm. The aqueous emulsion polymer contained a large amount of wet grit (0.18% of batch size).

Table 2

Emulsion Polymer	Early Block (24 hr)			Block (5 day)			Wet Adhesion				CRG
	20°	60°	RT <sup>1</sup>	Hot <sup>2</sup>	RT <sup>1</sup>	Hot <sup>2</sup>	10° Peel	10° XH <sup>4</sup>	WS <sup>5</sup>	24h	
Ex. 5	28	74	6.5	0	9	0	5	10	/	/	2000+
Ex. 6	45	83	6	2	8	3	5	9	/	/	2000+
Ex. 7	42	82	3.5	0	6	0	6	9	/	/	2000+
Ex. 8	23	71	9.5	3	10	-	9	10	/	/	2000+
Comp. Ex. 1	30	72	7	3	6	1	2.5	0	8D <sup>3</sup>	69	
SAMPLE											CELLED
Comp. Ex. 2	PAINT										
Comp. Ex. 3	39	80	8.5	2	9	3	8	8	/	/	2000+
Comp. Ex. 4	37	78	0	0	5	0	10	8	/	/	470
Comp. Ex. 5	44	82	6	4.5	7	7	8	8	/	/	940

<sup>1</sup> RT = room temperature<sup>2</sup> 120°F<sup>3</sup> blisters<sup>4</sup> XH = crosshatch <sup>5</sup> WS = watersoak / - no blisters observed

The results set forth above illustrate that coatings made with the aqueous two-stage emulsion polymers of this invention have reasonably good high gloss and wet adhesion properties.

5

The minimum film formation temperature was obtained for the aqueous two-stage emulsion polymer of Example 1 (22°C) and the single-stage aqueous emulsion polymer of Comparative Example 3 (39°C). The results show that

10 the aqueous two-stage emulsion polymer of this invention has an advantageously lower minimum film formation temperature compared to single-stage aqueous emulsion polymers.

15 Other variations and modifications of this invention will be obvious to those skilled in the art. This invention is not to be limited except as set forth in the following claims.

WHAT IS CLAIMED IS:

1. An aqueous two-stage emulsion polymer comprising:
  - (a) a first stage polymer having a calculated glass transition temperature of at least 70°C which is an addition polymer of at least one ethylenically unsaturated monomer; and
    - (b) a second stage polymer having a calculated glass transition temperature of from about 5° to about 50°C which is an addition polymer of at least one ethylenically unsaturated monomer which second stage polymer was polymerized in the presence of the first stage polymer, said second stage polymer further including at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate when the emulsion polymer is used in a paint composition and provided that said second stage polymer contains less than 4% by weight of ethylenically unsaturated monomer having carboxylic acid functionality; in
      - (c) an aqueous medium;wherein the weight ratio of the first stage polymer to the second stage polymer is in the range of from about 10:90 to 50:50 and the emulsion polymer has an average number particle size in the range of from about 60 to 250 nanometers.
  2. An aqueous two-stage emulsion polymer comprising:
    - (a) a first stage polymer having a calculated glass transition temperature of at least 70°C which is an emulsion polymerized addition polymer of at least one ethylenically unsaturated monomer having an average particle size in the range of from about 40 to 100 nanometers; and
      - (b) a second stage polymer having a calculated glass transition temperature of from about 5° to about 50°C which is an addition polymer of at least one

ethylenically unsaturated monomer which second stage polymer was polymerized in the presence of the first stage polymer, said second stage polymer further including at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate when the emulsion polymer is used in a paint composition and provided that said second stage polymer contains less than 4% by weight of ethylenically unsaturated monomer having carboxylic acid functionality; in

(c) an aqueous medium;

wherein the weight ratio of the first stage polymer to the second stage polymer is in the range of from about 10:90 to 50:50 and the emulsion polymer has an average particle in the range of from about 60 to 250 nanometers.

3. An emulsion polymer of Claim 1, wherein the glass transition temperature of the first stage polymer is at least 90°C, the calculated glass transition temperature of the second stage polymer is from about 10° to 40°C, and the average particle size of the emulsion polymer is in the range of from about 80 to 200 nanometers.

4. An emulsion polymer of Claim 2, wherein the glass transition temperature of the first stage polymer is at least 90°C, the calculated glass transition temperature of the second stage polymer is from about 10° to 40°C, and the average particle size of the emulsion polymer is in the range of from about 80 to 200 nanometers.

5. An emulsion polymer of Claim 3, wherein the ratio of the first stage polymer to the second stage polymer is from about 15:85 to 50:50.

6. An emulsion polymer of Claim 4, wherein the ratio of the first stage polymer to the second stage polymer is from about 15:85 to 50:50.

7. An emulsion polymer of Claim 5, wherein the calculated glass transition temperature of the first stage polymer is between about 90°C and 150°C.

8. An emulsion polymer of Claim 6, wherein the calculated glass transition temperature of the first stage polymer is between about 90°C and 150°C.

9. An emulsion polymer of Claim 1, wherein the ethylenically unsaturated monomers other than the monomer that promotes adhesion are selected from the group consisting of  $C_2$  to  $C_{20}$  alkenes,  $C_3$  to  $C_{20}$  alkadienes,  $C_5$  to  $C_{20}$  alkatrienes,  $C_6$  to  $C_{20}$  cycloolefins, vinyl substituted aromatics, acrylic or methacrylic acid,  $C_1$  to  $C_{20}$  alkyl esters of acrylic acid or methacrylic acid,  $C_6$  to  $C_{20}$  aryl esters of acrylic or methacrylic acid and  $C_1$  to  $C_{20}$  aralkyl esters of acrylic or methacrylic acid.

10. An emulsion polymer of Claim 2, wherein the ethylenically unsaturated monomers other than the monomer that promotes adhesion are selected from the group consisting of  $C_2$  to  $C_{20}$  alkenes,  $C_3$  to  $C_{20}$  alkadienes,  $C_5$  to  $C_{20}$  alkatrienes,  $C_6$  to  $C_{20}$  cycloolefins, vinyl substituted aromatics, acrylic or methacrylic acid,  $C_1$  to  $C_{20}$  alkyl esters of acrylic acid or methacrylic acid,  $C_6$  to  $C_{20}$  aryl esters of acrylic or methacrylic acid and  $C_1$  to  $C_{20}$  aralkyl esters of acrylic or methacrylic acid.

11. An emulsion polymer of Claim 1, wherein the monomer that promotes adhesion is an ethylenically

unsaturated monomer having an amino, ureido, or N-heterocyclic group.

12. An emulsion polymer of Claim 2, wherein the monomer that promotes adhesion is an ethylenically unsaturated monomer having an amino, ureido or N-heterocyclic group.

13. An emulsion polymer blend comprising a two-stage emulsion polymer according to Claim 1 and an emulsion polymer prepared with a low molecular weight acid functional support resin.

14. A coating composition comprising the two-stage emulsion polymer according to Claim 1 and a coalescent solvent.

15. A coating composition comprising the emulsion polymer blend according to Claim 13 and a coalescent solvent.

16. A method of making an aqueous two-stage emulsion polymer comprising the steps of

(a) emulsion polymerizing at least one ethylenically unsaturated monomer to form a first stage polymer having an average particle size of from about 40 to 100 nanometers wherein the first stage polymer has a calculated glass transition temperature of at least 70°C; followed by

(b) emulsion polymerizing in the presence of the first stage polymer at least one ethylenically unsaturated monomer having a functional group that promotes adhesion to a substrate when the emulsion polymer is used in a paint composition in conjunction with at least one ethylenically unsaturated monomer to form a second-stage polymer associated with the first stage polymer wherein the calculated glass transition

temperature, exclusive of the monomer that promotes adhesion, is in the range of from about 5° to about 50°C, provided that the second stage polymer contains less than 4% by weight of ethylenically unsaturated monomer having carboxylic acid functionality;

wherein the weight ratio of the first stage polymer to the second stage polymer is in the range of from about 10:90 to 50:50 and the emulsion polymer has an average particle in the range of from about 60 to 250 nanometers.

17. A method according to claim 16, wherein the steps of emulsion polymerizing are conducted at a polymerization reaction temperature in a range between about 40° to about 90°C.

18. A method according to claim 16, further comprising, prior to step (a), the step of emulsion polymerizing at least one ethylenically unsaturated monomer to form a seed polymer having a number average particle size between about 40 and about 90 nm.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F265/06 C08F291/00 C08F291/02 C09D151/00

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 376 096 A (ROEHM GMBH) 4 July 1990	1-10, 16, 17
Y	* page 5, line 20 - page 6, line 4 * see abstract ---	11-15, 18
X	US 4 683 269 A (AKSMAN IGOR B) 28 July 1987 cited in the application * column 2, line 26 - 30 ; column 2, line 48 - 55 ; column 2, line 14 - 20 ; column 3, line 48 - 55 * see examples 1-4 ---	1-10, 14, 16, 17
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 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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2

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/15130

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 97/15130

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